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Process Wastewater Treatability Study for Westinghouse Fluidized-Bed Coal Gasification

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16. ABSTRACT The paper discusses a joint program (The U.S. Department of Energy, the Gas Research Institute, and the U.S. Environmental Protection Agency) to develop performance data, design parameters, conceptual designs, and cost estimates for treating wastewaters from a fluidized-bed coal gasification plant. Preliminary results indicate that wastewater can be effectively treated by current technology. At this time the unit operations being evaluated are performing according to expectations. Results from bench-scale studies represent a first step in the development of a basis of design for treating these wastewaters. These data will also be used to develop conceptual designs from which cost estimates for wastewater treatment for a commercial-scale fluidized-bed coal gasification facility will be prepared.

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PROCESS WASTEWATER TREATABILITY STUDY FOR WESTINGHOUSE FLUIDIZED-BED COAL GASIFICATION

In the development of a synthetic fuels facility, water usage and wastewater treatment are major areas of concern. Coal gasification processes generally produce relatively large volumes of gas condensates. These wastewaters are typically composed of a variety of suspended and dissolved organic and inorganic solids and dissolved gaseous contaminants. Fluidized-bed coal gasification (FBG) processes are no exception to this rule.

The Department of Energy's Morgantown Energy Technology Center (METC), the Gas Research Institute (GRI), and the Environmental Protection Agency (EPA/IERL-RTP) recognized the need for a FBG treatment program to provide process design data for FBG wastewaters during the environmental, health, and safety characterization of the Westinghouse Process Development Unit (PDU). In response to this need, METC developed conceptual designs and a program plan to obtain process design and performance data for treating wastewater from commercial-scale Westinghouse-based synfuels plants. As a result of this plan, METC, GRI, and EPA entered into a joint program to develop performance data, design parameters, conceptual designs, and cost estimates for treating wastewaters from a FBG plant. Wastewater from the Westinghouse PDU consists of process quench and gas cooling condensates which are similar to those produced by other FBG processes such as U-Gas, and entrained-bed gasification processes such as Texaco. Therefore, wastewater from this facility was selected as the basis for this study. This paper outlines the current program for developing process design and cost data for the treatment of these wastewaters.

PROGRAM OBJECTIVES

The overall goal of this program is to obtain reliable data for input to conceptual designs for wastewater treatment facilities in commercial-scale, FBG plants. To satisfy this goal, the following objectives will be accomplished:

- Demonstrate that the wastewater can be treated in an environmentally acceptable manner using proven commercial treatment technologies.
- Obtain reliable unit operation performance data for treating wastewater from a Westinghouse-based plant.
- Obtain environmental characterization data on wastewater treatment system effluent and secondary discharge streams (gaseous, liquid, and solid).
- Develop kinetic and mass transfer relationships for incorporation into wastewater treatment unit operation design equations and for calculating full-scale unit operation performance.
- Prepare two example conceptual designs (e.g., heat and mass balances) for a wastewater treatment facility in a commercial-scale Westinghouse-based plant.
- Size major equipment items for the conceptual designs, and prepare preliminary cost estimates.

In this program a base-case plant configuration is used to identify other waste streams that require incorporation into a fully integrated water system. These streams will be included in the conceptual designs developed for a Westinghouse-based gasification facility.

APPROACH TO WASTEWATER TREATMENT

The approach to wastewater treatment at a synthetic fuels facility is based on several technical and site-specific considerations, such as:

- water/wastewater sources, flow, and compositions;
- performance capabilities and costs of candidate water treatment technologies;
- treatment objectives (e.g., recycle or discharge);
- effects of wastewater treatment systems on air pollution and solid waste management systems, and
- effects of wastewater treatment systems on the plant water balance and design/performance of other processing steps.

The water/wastewater flows and characteristics, treatment process performance capabilities, and treatment costs provide the basis for the development of an integrated water system. Two treatment objectives are considered in the conceptual design phase of the program: maximum reuse/recycle and discharge to surface water. These treatment objectives represent the range of ultimate wastewater disposal options available to the synfuels facility designer. The water quality required to achieve these objectives serve as target values to be attained by the development of a conceptual wastewater treatment system.

Figure 1 presents the primary sources of wastewater from a Westinghouse-based system producing a synthesis gas. This synthesis gas can be used for the production of fuel-grade methanol, SNG, and other products. The water sources from the main process train include:

- coal pile runoff (Stream 1),
- blowdown from the gasifier ash handling/sluicing system (Stream 2),
- quench liquor (Stream 3),
- gas cooling condensate (Stream 4),
- acid gas removal condensate (Stream 5),
- sulfur recovery wastewater (Stream 6), and
- sulfur storage runoff (Stream 7).

Where the synthesis gas is used to produce fuel-grade methanol or SNG, synthesis by-product wastewater and methanation condensate are additional wastewater streams that will be produced from the main process train. The compositions and flow rates of most of these streams are strongly influenced by a number of variables including: characteristics of feed coal, gasifier operating conditions, gas quench/cooling system design, gas upgrading, and the synthesis process(es) used.

The Westinghouse PDU produces two process related wastewater streams: quench liquor (Stream 3) and process gas cooling condensate (Stream 4). These streams represent the two largest volume process wastewater flows that would be produced at a typical FBG facility. Tables 1 and 2 present the composition of a blend of these two wastewater streams produced from the gasification of four different feedstocks. The sample was blended in proportion to the ratio at which both streams are produced. Trace element analysis has not been completed as yet. The relatively high suspended solids, ammonia, and cyanide concentrations indicate that extensive treatment of these streams will probably be required in order to meet typical discharge permit limitations or minimize impacts on other processes to which the water is recycled. Wastewater treatment processes specifically designed to remove these contaminants were selected for the bench-scale treatability studies.

The most significant organic constituent identified thus far is formate. Of the 10 organic priority pollutants, the only compound not found in the microgram/liter concentration range is naphthalene at 11 mg/l. At these low concentrations, removal of organics should not pose a significant problem. Further wastewater characterization in the program may indicate other contaminants such as trace elements that require additional treatment. The need for additional pilot testing will be considered where these contaminants are found to be significant.

Treatment of Sequences and Process Selection

The quench and product gas cooling condensate contain a variety of inorganic, organic, and dissolved gaseous contaminants. To remove these contaminants, a number of treatment steps must be undertaken. The processes selected and the sequence of treatment are dependent on the treatment objectives for a system. For this program, two treatment objectives are considered: discharge to surface waters and maximum recycle. Typical effluent quality goals established for discharge of treated wastewater are shown in Table 3 for the Mid-South Synfuels (U-Gas) coal gasification plant established by the State of Tennessee, DOE estimates for other synfuels plants, and the Petroleum Refining BPT. These examples show concentrations of various chemical species that could be regulated in a discharge permit. Quality goals for maximum reuse are dependent on the requirements of the system to which the treated wastewater is returned.

The treatment processes selected for bench-scale evaluation are summarized in Table 4. These treatment technologies represent some of the most common and reliable processes for the removal of suspended solids and nitrogen compounds and for concentration of process wastewaters that have been demonstrated on a commercial basis. The major tests are broken down into their components, and the function of each component is also presented in the table. For example, the reactor/clarifier has five components designed to convert or complex cyanide, coagulate and settle suspended solids and trace elements, and polish the treated effluent with filtration. Typical physical and chemical data to be taken for each unit operation are summarized in Tables 5 and 6. These data will provide the basic design/performance information on each treatment process.

The sequence of treatment may vary, depending on the treatment objective and the composition of the wastewater stream. Figure 2 presents a logic diagram identifying the major treatment scheme sequences that may be encountered at a Westinghouse-based gasification facility. The diamonds represent decision points where selection of operating conditions are made. The decision points are typical of those required to develop an overall conceptual design for treatment of different quality wastewaters to meet the two treatment objectives. The cyanide conversion treatment processes may be placed in a different order, depending on the wastewater composition, sensitivity of downstream processes, and overall treatment objectives for a system.

The logic diagram also indicates how the operating conditions selected for one treatment process can affect downstream processes. To demonstrate this, assume that a wastewater containing 30 mg/l of cyanide, 1000 mg/l of ammonia, and 5 weight percent suspended solids is to be treated by the scheme in the logic diagram to a point where the water can be discharged to surface waters (see darkened path on Figure 2). At Decision Point 1, the method of cyanide conversion or complexing must be selected. If cyanide complexing is selected, this automatically dictates that ion exchange must be used at Decision Point 4 to remove the complexed cyanide. At Decision Point 2, the choice of coagulants must be made. If pH is not increased during coagulation and clarification, then Decision Point 3 must be considered to ensure that the effluent ammonia levels are low enough to meet activated sludge feed requirements. If no pH adjustment is required, then steam stripping of the wastewater can be used. After ion exchange, Decision Point 5 considers the quality of the treated wastewater stream. If the quality of the wastewater meets permit limitations, then the water can be discharged to a surface water.

Preliminary Results

Preliminary results indicate that wastewater can be effectively treated by current technology. At this time the unit operations being evaluated are performing according to expectations. The results from the bench-scale studies represent a first step in the development of a basis of design for treatment of these wastewaters. These data will also be used to develop conceptual designs from which cost estimates for wastewater treatment for a commercial-scale fluidized-bed gasification facility will be prepared.

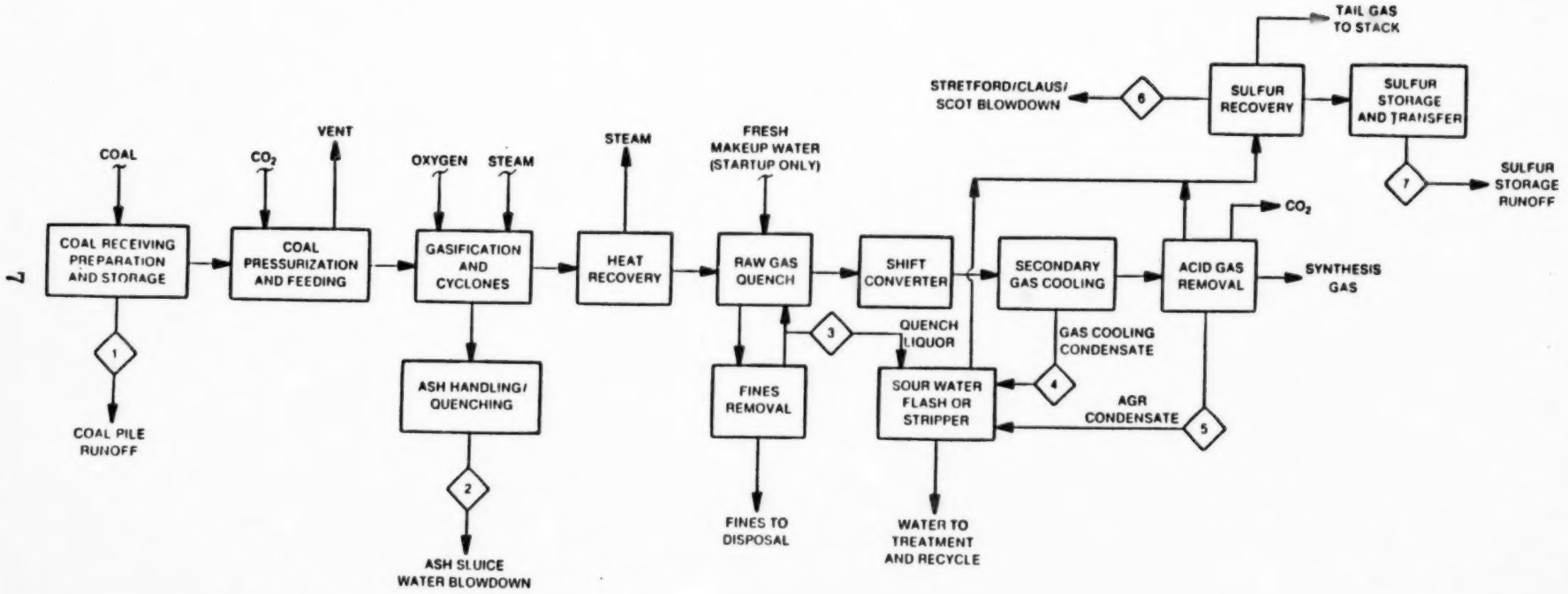
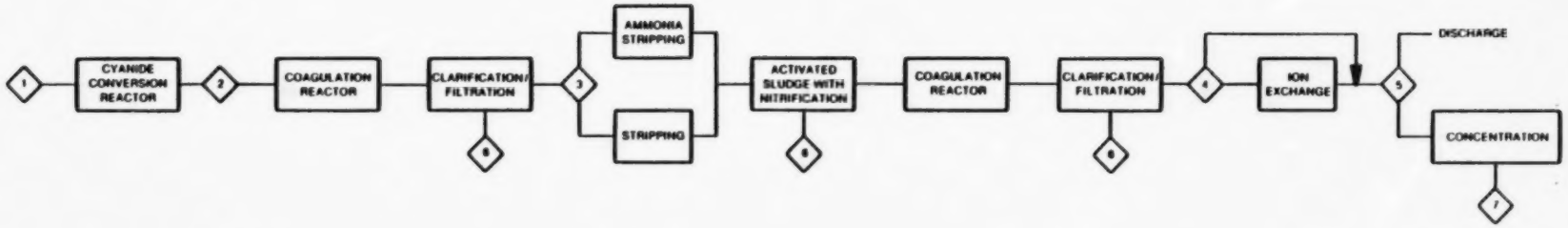


Figure 1. Sources of Process Waste Streams from a Westinghouse-Based Facility



1
- SELECTION OF STRIPPER PRETREATMENT APPROACH
- CONSIDER OTHER WASTE STREAMS THAT MAY BE COMBINED FOR TREATMENT
- SELECTION OF CYANIDE CONVERSION OR COMPLEXING BEFORE OR AFTER SUSPENDED SOLIDS REMOVAL

2
- SELECTION OF COAGULANT
- DETERMINE IF pH ADJUSTMENT REQUIRED
- SELECTION OF SEPARATE OR COMBINED REACTORS FOR CYANIDE CONVERSION/ COAGULATION

3
- DETERMINE IF pH ADJUSTMENT REQUIRED (MAY BE SET IN STEP 2)
- CONSIDER ANY OTHER WASTE STREAMS THAT MAY BE COMBINED FOR TREATMENT UP OR DOWN STREAM OF STRIPPER

4
- SELECTION OF ION EXCHANGE IF CYANIDE IS COMPLEXED

5
- SELECTION OF DISCHARGE OR ZERO DISCHARGE APPROACH
- CONSIDER ANY OTHER WASTE STREAMS THAT MAY BE COMBINED FOR TREATMENT PRIOR TO DISCHARGE OR REUSE

6
- SELECTION OF SLUDGE OR BACKWASH DISPOSAL METHOD

7
- SELECTION OF REGENERATION OR CONCENTRATED WASTE DISPOSAL METHOD

Figure 2. Fluidized-Bed Gasification Wastewater Treatment Logic Diagram

TABLE 1. WATER QUALITY ANALYSIS RESULTS: BLEND OF QUENCH AND PROCESS GAS COOLING CONDENSATE

Constituent	Range of Results[a]	Units
pH	7.8-8.7[b]	pH units
Conductivity	4,400-21,000[b]	µmhos/cm
Total Suspended Solids at 105°C	0.5-7.7	weight %
Total Dissolved Solids at 180°C	360-1,000	mg/l
Total Alkalinity as $CaCO_3$	1,600-8,200	mg/l
Chloride as Cl	30-620	mg/l
Flouride as F	6-21	mg/l
Ammonia as N	500-3,800[b]	mg/l
Cyanide as CN	31-55	mg/l
Thiocyanate as SCN	54-100[b]	mg/l
Total Phosphate	0.14-0.28	mg/l
Sulfide as S	21-100[b]	mg/l
Sulfite as SO_3	10-100[b]	mg/l
Sulfate as SO_4	90-280	mg/l
Biochemical Oxygen Demand	$\leq$150	mg/l
Chemical Oxygen Demand	130-350	mg/l
Total Organic Carbon	60-180	mg/l
Total Inorganic Carbon	270-1900	mg/l
Formate	15-110	mg/l

[a]The ranges of results are from samples collected at the Westinghouse PDU during the gasification of Western Kentucky No.9 Bituminous in December 1982 (TP-033-2), Wyoming Sub-bituminous in April 1983 (TP-034-1), Pittsburgh No.8 Bituminous in June 1983 (TP-034-2), and North Dakota Lignite in August 1983 (TP-034-3).

[b]Indicates that preliminary analyses from North Dakota lignite gasification is also included in the range.

TABLE 2. ORGANIC ANALYSIS RESULTS: BLEND OF QUENCH AND PROCESS GAS COOLER RECYCLE WATER[a]

Constituent	Results (µg/l)
Acid Fraction	
Phenol	48
Base/Neutral Fraction	
Acenaphthene	110
Fluoranthene	13
Bis(2-ethylehexyl) phthalate[b]	6
Diethyl phthalate[b]	5
Acenaphthylene	250
Naphthalene	11,000
Fluorene	88
Phenanthrene B	110
Pyrene	66
Volatile Organics	
Benzene	100

[a]Results for samples collected in December 1982 at the Westinghouse PDU during gasification of Western Kentucky No. 9 Bituminous (TP-033-2).

[b]Common contaminant not necessarily process wastewater related.

TABLE 3. EXAMPLE EFFLUENT QUALITY GOALS[a]

Constituent	Memphis BAT Effluent Limitations[b] (mg/l)	DOE Estimate for Synfuels Facilities[c] (mg/l)	Petroleum Refining BPT (mg/l)
GENERAL			
TDS	-[d]	500-5000	-
Color	Absent	Absent	-
Odor	Absent	Absent	-
TSS	25	-	15
ORGANIC INDICATORS			
BOD	10	10-30	20(max)
COD	100	30-300	200
Oil & Grease	10	1-10	5
Total Phenols	0.2	0.05-0.2	-
NITROGEN/SULFUR SPECIES			
NH_3	-	1-10	10
Nitrates & Nitrites (as N)	250	-	-
Total Cyanide	0.02	0.02-0.2	<0.1
$S^=$	-	0.03-0.3	0.1
TRACE ELEMENTS			
As	0.05	10^{-6}-10^{-3}	-
B	-	0.5-5	-
Cd	-	0.001-0.1	-
Cr (Total)	-	-	0.2
Hg	0.005	0.0005-0.005	-
Pb	-	0.005-0.5	-
Se	0.02	0.001-0.1	-
Zn	0.3	-	-
TOXIC ORGANIC COMPOUNDS			
Benzene	0.1	-	-
Toluene	0.1	-	-
Ethyl benzene	0.2	-	-
Phenol	0.1	-	0.05
Individual PAH	-	10^{-6}-10^{-3}	-

[a] Permit limitations may be more stringent for specific species. These effluent quality goals are only indicators of possible effluent guideline concentrations.

[b] Mid-South Synfuels, Incorporated which discharges to a publicly owned treatment works.

[c] Source: Processing Needs and Methodology for Wastewaters from the Conversion of Coal, Oil Shale, and Biomass to Synfuels, DOE/EV-0081, May 1980.

[d] No effluent quality goals have been established.

TABLE 4. TREATMENT PROCESSES SELECTED FOR UNIT OPERATIONS TESTS

Treatment Process Description	Test Component	Component Function
Reactor/Clarifier	Cyanide Conversion	Conversion of cyanide to thiocyanate
	Cyanide Complexing	Conversion of cyanide to a ferrocyanide complex
	Coagulation	Suspended solids and trace element removal
	Clarification	Suspended solids and trace element removal
	Filtration[a]	Suspended solids removal
Steam Stripping	Steam Stripping with no pH Adjustment	Removal of acid gases, ammonia, and volatile organics
Ammonia Stripping	Steam Stripping with pH Adjustment	Removal of ammonia and volatile organics
Activated Sludge with Nitrification		Removal of nitrogen compounds and low level organics. Oxidation of sulfide to sulfate
Ion Exchange		Removal of ferrocyanide complex
Concentration	Cooling Tower Concentration	Wastewater concentration
	Boiling Concentration	Wastewater concentration

[a]Filtration system design data will not be developed. Wastewater will be filtered where required to minimize the effects of suspended solids on other unit operations.

TABLE 5. WASTEWATER TREATMENT UNIT OPERATION PERFORMANCE DATA

	Reactor/Clarifier[a]	Stripping[b]	Activated Sludge	Ion Exchange	Concentration
COD	X	X	X		X
TOC			X		X
TKN		X	X		
Ammonia		X	X	X	
Nitrate/Nitrite			X	X	
Cyanide	X	X	X	X	
Thiocyanate	X	X	X	X	
Phenols			X		
Alkalinity	X	X	X	X	
pH	X	X	X	X	X
TSS/TVS	X		X		X
MLSS/MLVSS			X		
TDS	X			X	X
Oxygen Uptake			X		
Temperature	X	X	X	X	X
Sludge Settleability	X		X		
Density, Viscosity	X	X	X	X	X
Conductivity	X	X	X	X	X
Flow Rates (Normal/Peak)	X	X	X	X	X
Pressure Drop		X		X	
Steam Requirements		X	X		X
Liquid/Gas Ratio		X			
Chemical Dosage	X	X			
Loading Rates	X	X	X	X	

[a] Includes sedimentation, coagulation, cyanide conversion and complexing, and filtration.

[b] Includes ammonia stripping.

TABLE 6. ENVIRONMENTAL CHARACTERIZATION DATA FOR WASTEWATER TREATMENT UNIT OPERATIONS SECONDARY WASTE STREAMS

	Reactor/ Clarifier	Stripping	Activated Sludge	Ion Exchange	Concentration
Gaseous Streams					
Fixed gases (CO, CO_2, H_2, O_2, N_2, CH_4)		X			
Water content		X			
Sulfur species (H_2S, COS, CS_2, SO_2, methyl/ethyl mercaptans, thiophenes)		X			
C_1 to C_6 hydrocarbons		X			
Nitrogen species (NH_3, HCN, SCN)		X			
Volatile organics (C_6 to C_{12} hydrocarbons)		X			
Condensable organics (C_8+ hydrocarbons)		X			
Trace elements[b]		X			
Liquid Streams					
Water quality parameters[a]	X	X	X	X	X
Extractable organics (C_8+ hydrocarbons)	X	X	X		X
Nonextractable organics (e.g., organics remaining after analytical extraction such as formates and other organic acids)	X	X	X		X
Trace elements[b]	X	X	X	X	X
Density, viscosity	X	X	X	X	X
Solid Streams (including sludges)					
Proximate/ultimate	X		X		
Trace elements	X		X		
Radionuclides (gross alpha and beta), total Ra (226 and 228)	X		X		
Physical properties (bulk density, permeability, compressive strength, morphology, surface area, size distribution)	X		X		
Extractable organics (C_8+ hydrocarbons)	X		X		
RCA leaching	X		X		
Neutral (ASTM) leaching (analysis of the leachate)	X		X		

[a] pH, conductivity, alkalinity, bicarbonate, carbonate, TOC, COD, BOD, phenols, oil and grease, chloride, fluoride, settleable solids, total solids, TSS, TDS, CN^-, SCN^-, TKN, NH_3, $SO_4^=$, $SO_3^=$, $S^=$.

[b] Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, F, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Ti, Tl, V, Zn.